Production of Organic Molecules from Carbon Dioxide via Photocatalysis on Colloidal Semiconductor Particles

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An unanswered question about the origins of life is the source of the fundamental organic molecules that constitute the building blocks of life. Our work has investigated the photoelectrochemical reduction of CO2 on mineral surfaces as a significant contribution to carbon fixation on prebiotic Earth and the growth of long-chain organic molecules. The operative principle is that, when a semiconducting mineral such as MnS or ZnS absorbs a photon of energy greater than the bandgap, an electron in the valence band is excited to the conduction band. These excited electrons have a sufficiently negative reduction potential to reduce CO2 to CO2·- radical. The CO2·- radical yields formate and also undergoes chain addition to form C2 and longer chain carbon-carbon compounds.

We have demonstrated that under ultraviolet irradiation colloidal particles of sphalerite (ZnS) and alabandite (MnS) chemically reduce aqueous CO2 to form organic molecules. Respective initial quantum efficiencies of 9.9% and 4.2% were measured for formate production at pH = 6.3. The reaction rate was sensitive to the pH of the solution, increasing with acidity for the pH range of 5 to 9. The relationship between reaction rate and measured particle surface charge indicated that the neutral carbon species H2CO3 or CO2(aq) is the dominant reactant. The formate production rate was proportional to the initial concentration of aqueous inorganic carbon, suggesting an absence of surface saturation for the dominant reactant. Measurements of total organic carbon showed that photoproducts other than formate also formed, which implied the formation of carbon-carbon coupling products. High molecular weight organic molecules were detected by aerosol mass spectrometry.

The likely presence of colloidal semiconductor particles in the oceans of the prebiotic Earth suggests that photochemical reactions on their surface could have played a significant role in the prebiotic synthesis of organic molecules. Other proposals are that organic molecules may have originated via spark discharge (lightning), hydrothermal vents, or cometary delivery. For the range of chemical conditions plausible during the Hadean, however, the carbon productivity of these processes is arguably insufficient to yield the necessary concentrations of organic molecules for life to originate. Given that there is no consensus on a single mechanism that will produce organic matter over a wide range of conditions, it remains important to consider alternative mechanisms, such as the thesis of photoelectrochemistry on mineral colloids.